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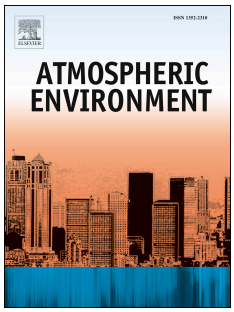

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Experimental Vapour Pressures of Eight n-Alkanes (C_{17}, C_{18}, C_{20}, C_{22}, C_{24}, C_{26}, C_{28} and C_{31}) Measured at Ambient Temperatures

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ABSTRACT

We present direct room-temperature vapour pressure measurements for eight semi-volatile n-alkanes of atmospheric importance. Measured vapour pressures range from 8.4 ±1.6 x 10^{-3} Pa for C_{17}, to 1.7 ±0.6 x 10^{-8} Pa for C_{31}. The new measurements for C_{17}-C_{18} are in reasonable agreement but at the lower end of values in the literature; the new measurements for C_{28} and C_{31} are one-to-two orders of magnitude higher than most literature values, but six orders of magnitude higher than the lowest values in the literature. Our measurements are suitable for atmospheric aerosol modelling and interpretation of environmental measurements, interpolated in carbon number where necessary, and extrapolated over temperatures relevant to the atmospheric boundary layer using the Clausius-Clapeyron equation with literature values of the enthalpy of vaporisation.

Keywords: Physico-chemical properties; vapour pressure; n-alkanes

1. INTRODUCTION

The equilibrium saturation vapour pressure (henceforth vapour pressure, p) of a compound is an intrinsic physical property related to its molar entropy and molar volume, and which plays a crucial role in determining a compound's transport behaviour in industrial, environmental, or biological media. Vapour pressure is defined as the pressure exerted by a pure substance, at a given temperature, in a system containing only the vapour and condensed phase (liquid or solid) of the substance at equilibrium (Calvert, 1990). The vapour pressure of a substance is highly dependent upon temperature through the Clapeyron and Clausius-Clapeyron equations (e.g. Atkins et al. 2018), and varies for different compounds of the same molecular mass due to molecular interactions (inter- and intramolecular in the condensed, and intramolecular in the vapour phase). For a substance to be in phase equilibrium, it must be in chemical, thermal and mechanical equilibrium (Bilde et al., 2015).

Many compounds of environmental interest - e.g., sulphuric acid, persistent organic pollutants, and (our focus in the current study) organic compounds derived from crude-oil fractionation — have small but environmentally important vapour pressures, the accurate measurement of which poses a significant experimental challenge, particularly for semi-volatile (1 to 10^{-6} Pa at room temperature) and 'non-volatile' (p <10^{-6} Pa) organic compounds. Given the exponential increase in the number of unique isomers possible as a function of carbon atoms in an organic molecule, the number of organic compounds in an atmospheric sample could be in the range of 10^{3} - 10^{4} (Goldstein and Galbally, 2007). Comparing these relative numbers with the experimental saturation vapour pressure literature available for atmospherically relevant organic molecules, it is evident that very limited data are available for low volatility and polyfunctional molecules, largely due to measurement challenges (Barley and McFiggins, 2010; Compernolle et al., 2011; Bilde et al., 2015). There are, however, well established experimental methods that provide good results at low pressures; for example the transpiration (Verevkin et al., 2000) and the Knudsen effusion techniques

(Dekruif and Vanginkel, 1077; Hallquist et al., 1997). Vapour pressure measurements have been conducted at ambient temperatures for few organic compounds using different techniques based upon the rate of evaporation of a compound under well controlled conditions (Razzouk et al., 2009; Cappa et al., 2007; Koponen et al., 2007). The majority of studies however, estimate *p* from experiments performed at high temperatures (Sawaya et al., 2006; O'Meara et al., 2014 and refs within), with subsequent extrapolation to ambient temperatures.

Ultrafine particles (UFP, with particle diameter Dp < 100 nm) in the urban atmosphere are dominated by particles composed of semi-volatile organic compounds (SVOC) (Harrison et al., 2011; Kumar et al., 2014). Accumulating evidence indicates that UFP are toxic and have potentially harmful effects on human health (Atkinson et al., 2010). In order to understand and model the atmospheric behaviour of SVOC, it is necessary to specify their chemical composition, their phase partitioning and the size distribution of the particulate fraction, and the vapour pressures of the constituent molecules (Harrison et al., 2019; Nikolova et al., 2018). Diesel exhaust vapour and particulate phases consist of SVOC in the range $C_{12} - C_{34}$ (Alam et al., 2016). Many of these SVOC in UFP have solid-liquid phase transitions at temperatures well above room temperature but are usually regarded as being present in UFP as super-cooled liquid mixtures. Thus, vapour pressures, at atmospherically relevant temperatures (i.e., approximately 240-310K for the near-surface atmosphere), are of fundamental importance for developing atmospheric and thermodynamic models Clegg et al., 2008). For unstudied compounds (usually those without industrial applications), numerous vapour pressure estimation techniques are available in the literature, based, for example, on structure-activity relationships. For compounds with industrial applications, experimental data for vapour pressures and thermodynamic quantities may exist but at much higher temperatures than found in the atmosphere (Barley and McFiggans, 2010). Vapour pressure estimation and extrapolation methods have recently been reviewed (Bilde et al., 2015; O'Meara et al., 2014; Barley and McFiggins, 2010). Since the measured thermodynamic property data are

scarce and mostly unavailable for atmospherically relevant compounds, these estimation methods are widely used as an approximation.

n-Alkanes are important constituents of the atmosphere, arising from both anthropogenic and biogenic sources (Dunmore et al., 2015; Harrad et al., 2003; Sartin et al., 2002; Fraser et al., 1997). Compounds from C_{10} to C_{30} partition between the vapour and condensed phases, and hence influence concentrations of airborne particulate matter (Fujitani et al., 2012; Lipsky and Robinson, 2006). C_{10} to C_{30} n-alkanes are important components of vehicle emissions, deriving from both diesel fuel and lubricating oil (Sakurai et al., 2003; Karjalainen et al., 2016; Alam et al., 2016). Prediction of the atmospheric behaviour of diesel exhaust particles requires knowledge of the physico-chemical properties of their chemical constituents, of which n-alkanes are among the most abundant (Harrison et al., 2016; Alam et al., 2018).

The majority of literature values of vapour pressure of the n-alkanes were estimated from extrapolation of vapour pressures measured at higher temperatures (Chirico et al., 1989; Morgan and Kobayashi, 1994; Sawaya et al., 2006; Razzouk et al. 2009). Very few studies have measured vapour pressures of n-alkanes at 298 K (Chickos and Hanshaw, 2004a; Chickos and Hanshaw, 2004b) and more recently extended measurements (and estimations) for n-alkanes up to n-C_{92} (Chickos et al., 2009). Although variability amongst reported vapour pressures is relatively small for the more volatile compounds, literature values for the lower volatility compounds can vary by more than five orders of magnitude for a single compound (see Figure 3 of Nikolova et al., 2018 and cf. Figure 1, below). With such a large range of extrapolated vapour pressures for a given compound, the behaviour of atmospheric models will depend greatly on which set of vapour pressures is adopted (Nikolova et al., 2018).

In this study, the transpiration method is adopted to make new measurements of vapour pressures of eight low volatility n-alkanes (C_{17}, C_{18}, C_{20}, C_{22}, C_{24}, C_{26}, C_{28} and C_{31}) at close to ambient

temperatures. In the transpiration method, a stream of nitrogen is slowly passed over the headspace above the pure n-alkane, picking up and transferring any material which is then trapped by a sorbent and analysed using comprehensive gas chromatography time-of-flight mass spectrometry. The vapour pressure is then calculated based on the mass of the compound transferred by the nitrogen gas stream (Verevkin et al., 2000).

2. EXPERIMENTAL

2.1 Experimental Setup

The experimental methodology was adopted from Verevkin et al. (2000) and is briefly described here. Individual n-alkane standards, C_{17}, C_{18}, C_{20}, C_{22}, C_{24}, C_{26}, C_{28} and C_{31} were purchased from Sigma Aldrich, UK (purity >99%). Approximately 0.5 g of the individual n-alkane was dissolved in dichloromethane (DCM, purity ≥99.9%; VWR International Ltd, UK) and ultrasonicated for 180 min at 298 K. The n-alkane was then coated onto 1 mm diameter glass beads; microscopy revealed the liquid coating to be present as a super-cooled liquid. Super-cooled liquid has a higher saturation vapour pressure than the more thermodynamically stable, but presumably kinetically hindered, crystalline solid. The coated beads were packed into a U-tube of length 20 cm and inner diameter 0.5 cm, and kept at a constant temperature of 298(±2)K, using a dry bath/block heater. A gentle flow of nitrogen (CP grade (N5.2) BOC, purity 99.9992%) was passed through the U-tube, such that contact time with the coated beads was long enough to allow the vapour to equilibrate with the pure liquid phase, after which the saturated vapour was stripped out of the nitrogen gas flow in a stainless steel thermal adsorption tube. Adsorption tubes (designed to collect SVOC from C_7 to C_{40}) were packed with 1 cm quartz wool, 300 mg Carbograph 2TD 40/60 (Markes International Ltd, UK), and were analysed using 2-dimensional Gas Chromatography Time of Flight Mass Spectrometry (GC×GC-ToFMS). The optimum flow rate of nitrogen used in these experiments was between 15.6 – 31.2 cm^3 min^{-1}, in order to not be too slow, thus avoiding transportation of material from the U-tube due to diffusion, and not too fast, to ensure saturation of the nitrogen flow with the

n-alkane (Verevkin et al. 2000). Assuming that the saturated nitrogen flow was subject to Dalton's law of partial pressures, the vapour pressure, *p* was calculated by assuming the validity of the ideal gas law (eq 1).

$$p = \frac{mRT}{V(total)MW} \approx \frac{mRT}{V(N_2)MW} \quad \text{(eq1)}$$

Where *p* is the vapour pressure (Pa), *m* is the mass of the measured n-alkane (g), *R* is 8.3144598 J K^{-1} mol^{-1}, *T* is temperature (K), *V*(*total*) is the total volume of gas sampled, which is closely approximated by $V(N_2)$, the calculated volume of N_2 (m^3) and *MW* is the molar mass (g mol^{-1}). The vapour pressure, *p*, was calculated from the mass of the n-alkane collected on the adsorption tube after the sampling time period. Each experiment was repeated five times with the exception of n-C_{31} (completed four times) as the time taken for this experiment was >10 days. Blanks were also sampled and all were below detection limit.

2.2 Analytical Instrumentation

Adsorption tubes were desorbed using thermal desorption (Unity 2, Markes International Ltd, UK) and subsequently analysed using a gas chromatograph (GC, 7890A, Agilent Technologies, USA) equipped with a Zoex ZX2 modulator (Houston, USA). The first dimension was equipped with a non-polar capillary column (SGE DBX5; 30 m, 0.25 mm ID, 0.25 µm – 5% phenyl polysilphenylene-siloxane), and the second dimension was equipped with a mid-polar capillary column (SGE DBX50; 4.0 m, 0.1 mm ID, 0.1 µm – 50% phenyl polysilphenylene-siloxane). The GC×GC was interfaced with a BenchTOF-Select, time-of-flight mass spectrometer (Markes International Ltd, UK) with a scan speed of 50 Hz and mass range 35 – 600 m/z. All data produced was processed using GC Image v2.5 (Zoex Corporation, USA). The adsorption tubes were spiked with 1 ng of deuterated internal standards, eicosane-d_{42} and pentacosane-d_{52} (Sigma Aldrich, UK),

for quantification and desorbed onto the cold trap at 380°C for 15 min (trap held at 20°C). The trap was then purged onto the first dimension column at 380°C and held for 3 min. The initial temperature of the primary oven was 80°C and then increased by 2.5°C min^{-1} to 320°C and held for 5 min. The initial temperature of the secondary oven was 80°C and was increased by 2.5°C min^{-1} to 150°C and then increased by 3.0°C min^{-1} to 330°C and held for 8 min. Helium was used as the carrier gas at a constant flow rate of 0.8 L min^{-1}.

Compounds were identified based on the NIST mass spectral library, known retention times and in conjunction with authentic standards. The quantification for n-alkanes was performed by the linear regression method using seven-point calibration curves established between the authentic standards/internal standard concentration ratios. The calibration curves for all n-alkanes were highly linear (r^2>0.99).

3. RESULTS AND DISCUSSION

The observed experimental vapour pressures are presented in Table 1, and illustrate the repeatability of the transpiration technique for measuring individual vapour pressures of n-alkanes. Due to the slight deviation in the temperature (296 – 300 K), the observed vapour pressures were adjusted to 298 K for each compound using the Clausius-Clapeyron equation, integrated assuming the enthalpy of vaporisation is independent of temperature over the range of the temperature correction (eq 2).

$$p_{298k} = \frac{p_i}{exp^{\left(\frac{\Delta H_{vap}}{R}\right)\left(\frac{1}{298}-\frac{1}{T_i}\right)}} \quad \text{(eq 2)}$$

Where p_{298K} is the vapour pressure at 298 K, p_i is the measured vapour pressure of n-alkane (i) at observed T (K), ΔH_{vap} is the enthalpy of vaporisation (obtained from Chickos and Hanshaw,.

2004a), or calculated using $\Delta H_{vap} = -3.82(\pm 0.03) \ln p_i + 70.0(\pm 0.2)$ adopted from Goss and Schwarzenbach (1999), R is the universal gas constant (8.3144598 J K^{-1} mol^{-1}) and T_i is the measured temperature during the experiment for specific n-alkane (i).

The ΔH_{vap} is a function of temperature and is not constant. Therefore, extrapolation of vapour pressures to higher temperatures or extrapolation from higher temperature data for a given compound to ambient temperatures leads to significant uncertainty. Unlike the majority of previously published literature (discussed herein), the experimental vapour pressures presented in Table 1 are made close to ambient temperatures (296 – 300 K) for all compounds and so the Clausius-Clapeyron equation can be used to adjust the presented vapour pressures to 298 K.

3.1 Comparison with Published Data

Figure 1 illustrates the absolute difference of $\log_{10}$ saturation vapour pressure between literature data and measurements made in our lab. Although, the vapour pressure data presented in this study are amongst the lowest for n-C_{17} and n-C_{18} alkanes in comparison to the literature, they are in reasonable agreement (see Figure 1). Similarly, the vapour pressure of n-C_{20} alkane is lower than the selected literature, but in excellent agreement with the estimation methods of Nannoolal et al. (2008) and Myrdal and Yalkowsky (1997) when using the boiling point of Joback and Reid (1997). There is very good agreement for n-C_{22} and n-C_{26} alkane vapour pressures when compared to the estimation method of Compernolle et al. (2008) and the experimentally determined pressures of Goss and Schwarzenbach (1999), Chickos and Hanshaw (2004a) and Morgan and Kobayashi (1994). For n-C_{24} and n-C_{28} alkanes, the experimental saturation vapour pressures are higher than the saturation vapour pressures among the selected literature and these two compounds do not well fit the linear trend seen in Figure 2. Their measured vapour pressures were, however, very repeatable (Table 1) and we have no reason to doubt the quality of the data. The saturation vapour pressure of n-C_{31} is in very good agreement with the estimation method of Compernolle et al. (2001) and the experimentally determined pressure reported by Chickos and Hanshaw (2004b), but

are relatively much higher than those estimated by Kudchadker and Zwolinski (1966), Nannoolal et al. (2008) and Myrdal and Yalkowsky (1997); the latter two studies using the boiling point of Joback and Reid (1987).

Kudchadker and Zwolinski (1966) report some of the lowest vapour pressures among the selected literature (see Figure 1). They use an extrapolation of existing experimental data (measured by the chemical and petroleum industries, at unreported but presumably much higher temperatures) for n-alkanes based on Antoine constants and the Kreglewski-Zwolinski correlation. The extrapolation capabilities of the Antoine equation are limited; particularly for low pressures and near the triple point, and it is usually utilised over a limited temperature range. Extrapolation of vapour pressure data using the Antoine equation should be avoided when temperature intervals for correlation exceed 50 K (Ruzicka and Majer ,1996). Their vapour pressures however, are in good agreement with those estimated by Nannoolal et al. (2008) and Mrydal and Yalkowsky (1997) when using the boiling point of Joback and Reid (1987). Ruzicka and Majer (1996) investigated four types of empirical relationships frequently used for correlation of vapour pressure data, including Antoine, Wagner, Quasi-polynomial and Cox equations. They demonstrated that the use of different types of correlation equations can considerably affect the results of the extrapolation, and indicated that the Antoine equation revealed the poorest performance, which is related to over-fitting of the vapour pressure data; a typical effect observed when using simple extrapolations with too many parameters. Morgan and Kobayashi (1994) reported direct vapour pressure measurements of ten n-alkanes in the C_{10} – C_{28} range, at temperatures between 323 and 588 K. Their data for n-C_{22} is in good agreement with this study but there is less agreement for the less volatile n-alkanes (n-C_{24} and n-C_{28}). This is due to the vapour pressures of the latter alkanes being measured at elevated temperatures (n-C_{24}: 453–588 K and n-C_{28}: 483–588 K). Vapour pressure data measured at the conditions of interest (298 K) have lower uncertainty than data that are extrapolated from significantly larger temperatures. The authors discuss that the accuracy of low pressure direct measurements can be affected by the inadequacy of the experimental method, phenomenological effects, and thermal decomposition.

Vapour pressure data can also be affected by small impurities within the pure n-alkane, particularly for the less volatile hydrocarbons, or vapours that may interfere with the measurements (e.g. impurities present in the carrier gas). Thermal decomposition is known to limit the accuracy of critical property measurements such as the critical pressure, critical temperature, melting and boiling points (Morgan and Kobayashi,1991). The study also used the Wagner vapour pressure equation to extrapolate between mid-pressure range data towards low reduced temperatures which limits the flexibility of the relationship in low-pressure extrapolations. Many studies have identified the Cox equation as the most reliable for extrapolation towards low temperatures as they offer the possibility of changing both the number of parameters and the reference temperature and pressure (Ruzicka and Majer, 1996). It is, therefore, not surprising that the reported vapour pressures in Chirico et al. (1989), Chickos and Hanshow (2004a) and Ruzicka and Majer (1993) are very similar, and in excellent agreement, particularly for the low molecular weight n-alkanes.

As the chain length of the n-alkanes increases, the intermolecular van der Waals forces increase, up until a chain length at which the sample can be vaporised only through rupture of the C-C bonds (Morgan and Kobayashi, 1991). This occurs typically close to C_{100}, where samples will have a melting point but no longer have a triple point. Most of the estimation methods reported in the literature require a normal boiling point that is used to extrapolate down to atmospherically relevant temperatures (Barley and McFiggans, 2010). Due to the high boiling point, small errors in the slope can produce substantial differences in the predicted vapour pressure, particularly for the low molecular weight compounds.

3.2 Use by Atmospheric Science Community

A number of estimation methods to calculate vapour pressures have been used in the atmospheric science community (Myrdal and Yalkowsky, 1997; Nannoolal et al., 2008; Compernolle et al., 2011; O'Meara et al., 2014). Myrdal and Yalkowsky, 1997 and Nannoolal et al. (2008) calculate vapour

pressures using the temperature boiling points of Joback and Reid (1987), Stein and Brown (1994) and Nannoolal et al (2004). For example UmanSysProp (http://umansysprop.seaes.manchester.ac.uk) is an online web-based facility for the prediction of properties of individual organic compounds (including sub-cooled liquid vapour pressure) using specific functional groups ((Topping et al., 2016). Under standard atmosphere conditions, the methods of Myrdal and Yalkowsky (1997) and Nannoolal et al. (2008) using Joback and Reid (1987) boiling points produce the lowest vapour pressures for the n-alkanes studied in comparison to the same methods but using the boiling point of Stein and Brown (1994), see Figure 2. The discrepancy is more evident for n > 20, where the deviations of the sub-cooled vapour pressure become very large. Many studies have reported that the method of Joback and Reid (1987) tends to over-predict the boiling points of the compounds measured in this study, and hence underestimates the slope of the vapour pressure curve (Clegg et al., 2008; Barley and McFiggans, 2010; Compernolle et al., 2011). On the other hand, the estimation of vapour pressure by Myrdal and Yalkowsky (1997) using the boiling point of Nannoolal et al. (2004) tends to overestimate vapour pressures (2010). Figure 2 illustrates the substantial range of estimated (and measured) vapour pressures for the studied n-alkanes. The disagreement between estimated vapour pressures of the same compound at high molecular weight (over 9 orders of magnitude) illustrates the need to directly measure vapour pressures at the conditions of interest, and show the difficulties in accurately extrapolating and predicting data at ambient temperatures. This is further discussed in Nikolova et al. (2018).

A new vapour pressure estimation method ('EVAPORATION') for zero-, mono- and poly-functional groups has recently been published (Compernolle et al., 2011). Although this method is particularly developed for oxidised biogenic molecules, it has been reported to produce accurate (O'Meara et al., 2014). O'Meara et al. (2014) in their assessment of vapour pressure estimates have compared the vapour pressure error of organic compounds based on seven methods, including

EVAPORATION. They show that the error in the vapour pressure among the 90 organic compounds is relatively small for the EVAPORATION method (running close to zero).

Overall, the technique described in this study gave repeatable measurements and vapour pressures intermediate between the highest and lowest values available from the literature, suggesting that the literature data were subject to random error, exacerbated by the large temperature extrapolation, rather than systematic bias. For atmospheric aerosol modelling and interpretation of environmental measurements we recommend direct use of our data, interpolated in carbon number where necessary, and extrapolated over temperatures relevant to the atmospheric boundary layer using equation (2), above. Of the existing parameterisations, we have used Compernolle et al. (2011) as base case in a recent modelling study (Nikolova et al., 2018) because it follows our direct measurements reasonably well.

DATA ACCESSIBILITY

Data supporting this publication are openly available from the UBIRA eData repository at https://doi.org/10.25500/eData.bham.00000292

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CONFLICTS OF INTEREST

There are no conflicts to declare.

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TABLES LEGENDS

Table 1: Saturation vapour pressure measurements for eight n-alkanes at ambient temperatures (K). Vapour pressures at 298K were calculated using (eq2) and the average vapour pressures reported with 1σ standard errors including error propagation through equation 2 of the main text. Vapour pressures at 298K were calculated with the use of ΔH_v^a (experimental: Chickos and Hanshaw (2004a)) and ΔH_v^b (calculated: Goss and Schwarzenbach, 1999).

FIGURE LEGENDS

Figure 1: Absolute error of $\log_{10}$ saturation vapour pressure between literature and our study. The n-alkanes are detailed in the legend. Abbreviations in the x-axis are as follows: (subscript 'e' denotes experimental studies): KU – Kudchadker and Zwolinski (1996), CHR – Chirico et al. (1989), MO – Morgan and Kobayashi (1994), RU – Ruzicka and Majer (1993), GO – Goss and Schwarzenbach (1999), CH1 – Chickos and Hanshaw (2004a), CH2 – Chickos and Hanshaw (2004b), N – Nannoolal et al. (2008), MY – Myrdal and Yalkowsky (1997), CO – Compernolle et al.(2011). Abbreviations in parenthesis point to the boiling point method, as follows: (JR) – Joback and Reid (1987), (SB) – Stein and Brown (1994), (N) – Nannoolal et al. (2004).

Figure 2. Vapour pressure data for selected n-alkanes at 298 K. Abbreviations in the legend are as follows: (subscript 'e' denotes experimental studies): KU – Kudchadker and Zwolinski (1996), CHR – Chirico et al. (1989), MO – Morgan and Kobayashi (1994), RU – Ruzicka and Majer (1993), GO – Goss and Schwarzenbach (1999), CH1 – Chickos and Hanshaw (2004a), CH2 – Chickos and Hanshaw (2004b), N – Nannoolal et al. (2008), MY – Myrdal and Yalkowsky (1997), CO – Compernolle et al.(2011), EPI Suite – U.S. Environmental Protection Agency calculator. Abbreviations in parenthesis point to the boiling point method, as follows: (JR) – Joback and Reid (1987), (SB) – Stein and Brown (1994), (N) – Nannoolal et al. (2004).

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n-C_{17} Alkane			
		ΔH_v^a (KJ/mol)	**ΔH_v^b (KJ/mol)**
		86.3 (±1.2)	88.86 (±0.28)
		At 298 K	
		Vapour Pressure, p / Pa (10^{-3})	
297.5	5.30	5.62	5.63
296.0	6.06	7.66	7.72
296.5	8.36	9.97	10.02
297.0	8.89	9.99	10.03
296.5	7.23	8.63	8.67
298		**8.37 (±1.63)**	**8.41 (±1.64)**

n-C_{18} Alkane			
		ΔH_v^a (KJ/mol)	**ΔH_v^b (KJ/mol)**
		91.1 (±1.3)	93.02 (±0.29)
		At 298 K	
		Vapour Pressure, p / Pa (10^{-3})	
300.0	2.78	2.18	2.17
299.0	2.13	1.89	1.88
298.5	2.59	2.43	2.43
298.5	2.53	2.38	2.38
297.0	1.87	2.12	2.12
298		**2.20 (±0.20)**	**2.20 (±0.20)**

n-C_{20} Alkane			
		ΔH_v^a (KJ/mol)	**ΔH_v^b (KJ/mol)**
		101.9 (±1.4)	99.21 (±0.32)
		At 298 K	
		Vapour Pressure, p / Pa (10^{-4})	
297.0	6.48	7.44	7.42
297.0	2.50	2.87	2.86
297.0	5.29	6.08	6.06
298.5	4.52	4.22	4.23
298.0	5.49	5.49	5.49
298		**5.22 (±1.57)**	**5.21 (±1.56)**

n-C_{22} Alkane			
		ΔH_v^a (KJ/mol)	**ΔH_v^b (KJ/mol)**
		111.9 (±2.7)	103.25 (±0.34)
		At 298 K	
		Vapour Pressure, p / Pa (10^{-4})	
298.0	0.75	0.75	0.75
298.0	1.61	1.61	1.61
298.0	2.49	2.49	2.49
298.5	2.07	1.92	1.93
298.5	1.71	1.59	1.60
298		**1.67 (±0.56)**	**1.67 (±0.57)**

n-C_{24} Alkane			
		ΔH_v^a (KJ/mol)	**ΔH_v^b (KJ/mol)**
		121.9 (±2.8)	101.63 (±0.32)
		At 298 K	
		Vapour Pressure, p / Pa (10^{-4})	
297.0	1.81	2.14	2.08
297.0	2.23	2.63	2.56
297.0	2.86	3.38	3.29
297.0	2.74	3.24	3.15

n-C_{26} Alkane			
		ΔH_v^a (KJ/mol)	**ΔH_v^b (KJ/mol)**
		131.7 (±3.2)	115.58(±0.39)
		At 298 K	
		Vapour Pressure, p / Pa (10^{-6})	
298.0	4.05	4.05	4.05
299.0	6.15	5.15	5.26
299.0	5.85	4.90	5.01
299.0	8.29	6.94	7.09

297.0	2.81	3.32	3.23
298		**2.94 (±0.48)**	**2.86 (±0.47)**

298.0	8.02	8.02	8.02
298	**0.00**	**5.81 (±1.45)**	**5.89 (±1.45)**

n-C_{28} Alkane

ΔH_v^a (KJ/mol)	ΔH_v^b (KJ/mol)
141.9 (±4.9)	108.66(±0.36)

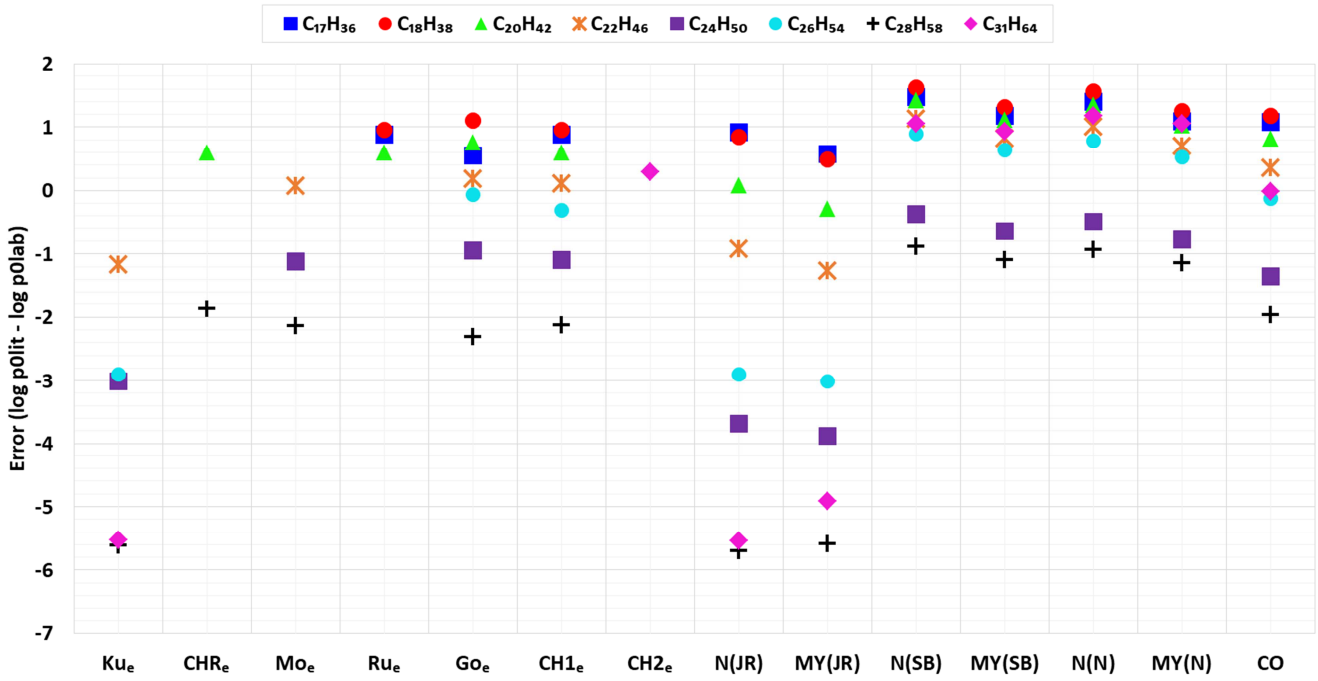
		At 298 K	
		Vapour Pressure, p / Pa (10^{-5})	
298.0	4.75	4.75	4.75
297.5	4.75	5.23	5.12
297.5	3.55	3.90	3.82
297.5	3.10	3.41	3.34
297.5	3.47	3.82	3.74
298		**4.23 (±0.67)**	**4.15 (±0.67)**

n-C_{31} Alkane

ΔH_v^a (KJ/mol)	ΔH_v^b (KJ/mol)
157.3 (±1.2)	139.00 (±0.48)

		At 298 K	
		Vapour Pressure, p / Pa (10^{-8})	
297.0	0.76	0.94	0.91
296.5	0.93	1.29	1.24
298.0	2.37	2.37	2.37
297.5	1.88	2.09	2.06
298		**1.67 (±0.58)**	**1.65 (±0.59)**

Footnote:
Column 1 - Temperature of each experiment
Column 2 - Vapour Pressure calculated at that temperature (in Column 1), using eq 1.
Column 3 - Vapour pressures at 298K using ΔH_v^a and Clausius-Clapeyron equation (eq 2). ΔH_v^a determined experimentally by Chickos and Hanshaw[34] (which are almost identical to the literature recommendations).
Column 4 - Vapour pressures at 298K using ΔH_v^b and Clausius-Clapeyron equation (eq 2). ΔH_v^b determined by using the simple equation in the manuscript text (Goss and Schwarzenbach[37].



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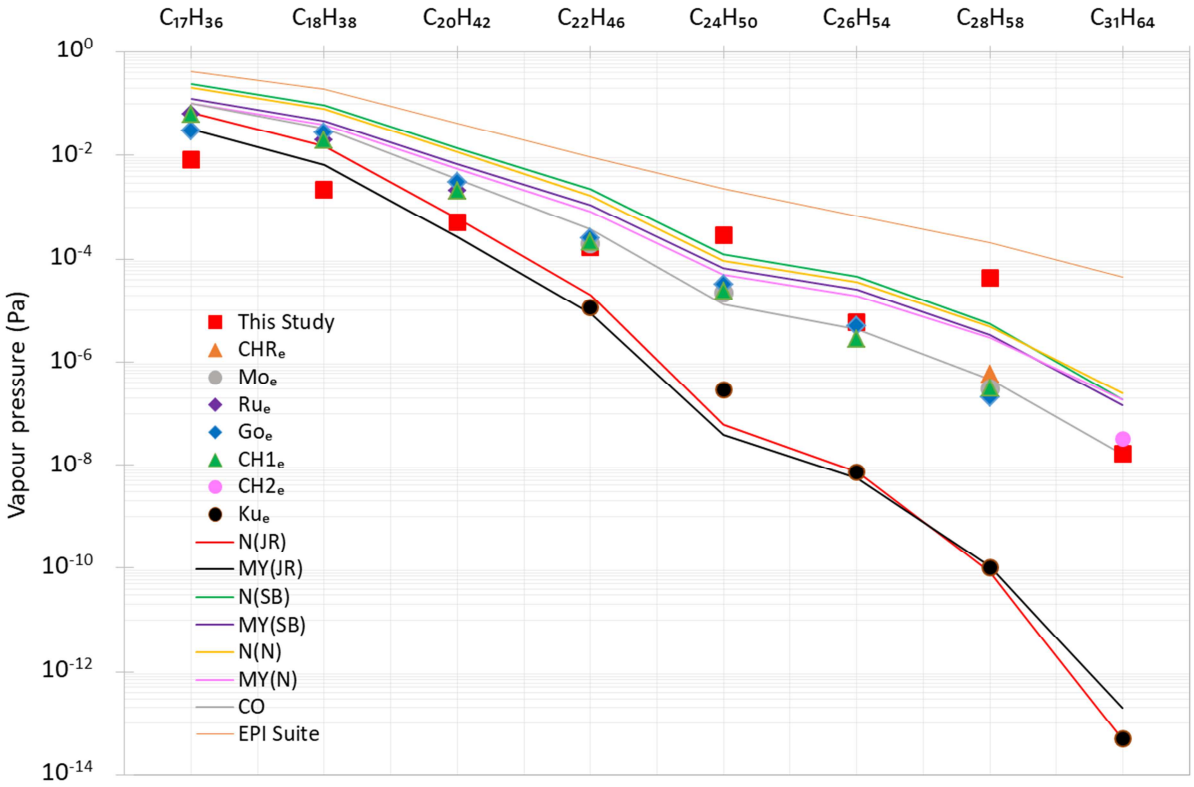
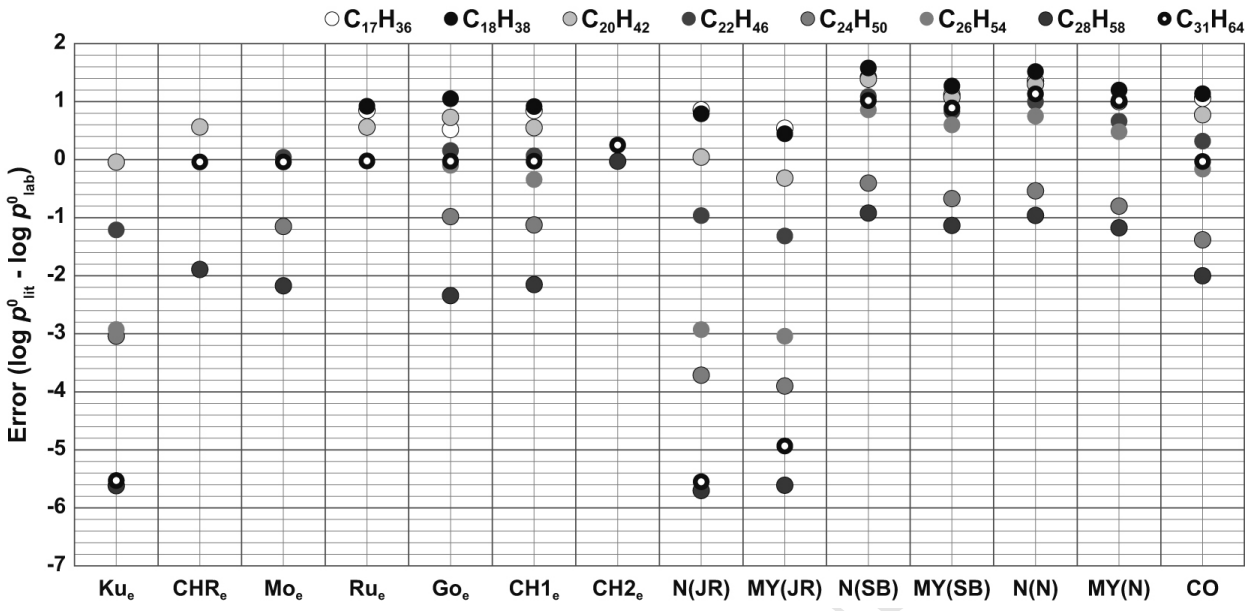


Figure 2. Vapour pressure data for selected n-alkanes at 298 K. Abbreviations in the legend are as follows: (subscript 'e' denotes experimental studies): KU – Kudchadker and Zwolinski (1996), CHR – Chirico et al. (1989), MO – Morgan and Kobayashi (1994), RU – Ruzicka and Majer (1993), GO – Goss and Schwarzenbach (1999), CH1 – Chickos and Hanshaw (2004a), CH2 – Chickos and Hanshaw (2004b), N – Nannoolal et al. (2008), MY – Myrdal and Yalkowsky (1997), CO – Compernolle et al.(2011), EPI Suite – U.S. Environmental Protection Agency calculator. Abbreviations in parenthesis point to the boiling point method, as follows: (JR) – Joback and Reid (1987), (SB) – Stein and Brown (1994), (N) – Nannoolal et al. (2004).



Experimental Vapour Pressures of Eight n-Alkanes (C_{17}, C_{18}, C_{20}, C_{22}, C_{24}, C_{26}, C_{28} and C_{31}) Measured at Ambient Temperatures

Mohammed S. Alam, Irina Nikolova, Ajit Singh, A.R. MacKenzie and Roy M. Harrison

HIGHLIGHTS

- High MW alkanes are semi-volatile and vapour pressure is an important property
- Reported individual vapour pressures range over up to 8 orders of magnitude
- New measurements are made at tropospheric ambient temperatures